

α -Sulfonated Fatty Acid Esters: II. Solution Behavior of α -Sulfonated Fatty Acid Polyethylene Glycol Esters

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ABSTRACT: Sodium α -sulfonated fatty acid polyethylene glycol monoesters [$C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)_nH$] and diesters [$C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)_nCOCH(SO_3Na)C_mH_{2m+1}$], where $m = 10$ – 16 and $n = 1$ – 35 , were prepared by esterification of α -sulfonated fatty acids with polyethylene glycols, followed by neutralization with NaOH. Crude products were purified by reversed-phase column chromatography on an octadecyl-modified silica gel. Characteristic solution behavior of these α -sulfonated fatty acid esters was examined, and the following features were observed. All monoesters prepared in this work had Krafft points below 0°C and also possessed good calcium stabilities. Critical micelle concentrations of the monoesters increased monotonously, as a rule, with an increase in the number of oxyethylene units. These results suggest that the polyethylene glycol residue of the monoester behaves as a hydrophile. On the other hand, diesters possessed high water solubility, low foamability, and critical micelle concentrations that were lower by a factor of ten compared to those of the monoesters. *JAACS* 73, 31–37 (1996).

KEY WORDS: Calcium stability, critical micelle concentration, foaming property, interfacial tension, Krafft point, polyethylene glycol diesters, polyethylene glycol monoesters, solution behavior, structural effect.

In a previous paper (1), structural effects of sodium α -sulfonated fatty acid higher-alcohol esters on surface-active properties were reported, where some characteristic features, such as low interfacial tension, good emulsifiability, and extremely low foaming properties were elucidated. Most of them, however, had relatively high Krafft points, perhaps resulting in restricted practical applications. A series of polyethylene glycol esters of sodium α -sulfonated fatty acid was then prepared to attain more hydrophilic character.

Esterification of polyethylene glycol and α -sulfonated fatty acid simultaneously produces monoester and diester. A molecule of sodium α -sulfonated fatty acid polyethylene glycol monoester consists of one hydrophobic alkyl chain and two hydrophilic residues, i.e., a nonionic oxyethylene (EO) unit and an anionic sulfonate group, located on the same carbon atom. The structure of the α -sulfonated fatty acid poly-

ethylene glycol monoester molecule is significantly different from alkyl ethoxy sulfate (AES), which has an anionic sulfate group attached to the end of the EO chain, and simultaneously possesses well-known and favorable surface-active properties (2,3). There are few studies, however, concerning sodium α -sulfonated fatty acid polyethylene glycol monoesters, except for the work by Micich *et al.* (4), which deals with sodium α -sulfonated palmitic and stearic acid monoethylene glycol monoesters.

Sodium α -sulfonated fatty acid polyethylene glycol diesters are examples of amphiphatic compounds with double lipophilic groups and double hydrophilic groups. Recently, such surfactants have been studied by Rosen, Okahara, and their coworkers (5–9), and many favorable features, such as low Krafft point and low critical micelle concentration (CMC), were determined.

In this paper, solution behavior of sodium α -sulfonated fatty acid polyethylene glycol mono- and diesters are presented and then related to structural features.

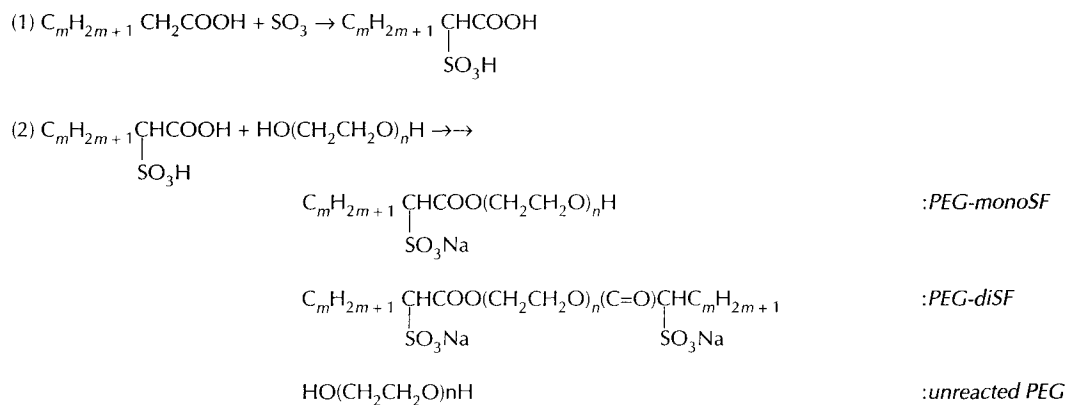
EXPERIMENTAL PROCEDURES

Materials. α -Sulfonated fatty acids ($m = 10$ – 16) were prepared according to the well-known method described in a previous paper (1). A mixture of α -sulfonated fatty acid, polyethylene glycol ($n = 1$ – 35) and carbon tetrachloride was refluxed, and water was azeotropically removed. Mono-, di-, and triethylene glycol used in these experiments were pure materials, while others had conventional molecular weight distributions. After evaporating the solvent, the esterification mixture was poured into a large excess of ethanol and neutralized by addition of aqueous sodium hydroxide. Two filtrations and concentrations produced a mixture that consisted of sodium α -sulfonated fatty acid polyethylene glycol monoester, diester, and unreacted raw materials (Scheme 1 shows the preparation of PEG=monoSF and PEG=diSF).

Typical procedures for the preparation of α -sulfonated fatty acid polyethylene glycol esters are as follows. For α -Sulfonated lauric acid triethylene glycol esters, a mixture of α -sulfonated lauric acid (28.0 g, 0.1 mol), prepared according to a method described in a previous paper (1), triethylene glycol (15.0 g, 0.1 mol), purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and carbon tetrachloride (500 mL) was refluxed for 5 h. Water was azeotropically removed

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SCHEME 1

during reflux. After solvent evaporation, the esterification mixture was poured into a large excess of ethanol and neutralized with aqueous sodium hydroxide. Two filtrations and concentrations gave a mixture that consisted of sodium α -sulfonated lauric acid triethylene glycol monoester, diester, and unreacted raw materials. Quantitative ratios of the components were determined by high-performance liquid chromatography (HPLC) separation technique. HPLC separations were conducted with a GL Science (Tokyo, Japan) Model 572P instrument connected to a GL Science Model 504 RI detector. Separations were performed on a Nucleosil-5SB (GL Science) anion exchange column (stainless steel, 15 cm \times 4.6 mm). The analyses were carried out isocratically with a mixture of methanol and water (8:2, vol/vol; flow rate, 0.8 mL/min) containing 0.8 wt% sodium perchlorate as the mobile phase at ambient temperature. For quantitative determinations, peak areas were calculated with a Labchart-180 integrator (System Instruments Co., Ltd., Tokyo, Japan). Retention times and quantitative ratios of sodium α -sulfonated lauric acid triethylene glycol monoester, diester, and unreacted triethylene glycol in the esterification mixture were as follows: 4.1 min, 48 wt% monoester; 10.8 min, 27 wt% diester; and 2.6 min, 25 wt% triethylene glycol. Separation and purification of the components were carried out by reversed-phase column chromatography on octadecyl-modified silica gel with a methanol-water (6:4, vol/vol) eluent. Purities of monoester (clear viscous liquid) and diester (white solid) were determined to be more than 95% with the same HPLC method mentioned above. Their structures were confirmed by Fourier transform infrared spectroscopy (FT-IR) System-2000 (Perkin-Elmer, Yokohama, Japan) and ^1H NMR JNM-GSX400 (JEOL, Tokyo, Japan). Spectral data of α -sulfonated lauric acid triethylene glycol monoester were as follows: IR (neat): 3,450, 2,920, 2,850, 1,742, 1,468, 1,379, 1,234, and 1,120 cm^{-1} ; ^1H NMR (in CDCl_3): 0.87 ppm (parts per million) ($-\text{CH}_3$:3H), 1.27 ppm ($-\text{CH}_2-\text{CHSO}_3\text{Na}$:2H), 3.64 ppm ($-\text{O}-\text{CH}_2$:10H), 3.96 ppm ($-\text{CH}_2-\text{CH}-\text{SO}_3\text{Na}$:1H), and 4.25 and 4.52 ppm ($-\text{COO}-\text{CH}_2$:2H). Spectral data of α -sul-

fonated lauric acid triethylene glycol diester was as follows: IR (KBr): 2,919, 2,850, 1,739, 1,467, 1,379, 1,234, and 1,120 cm^{-1} ; ^1H NMR (in CDCl_3): 0.87 ppm ($-\text{CH}_3$:6H), 1.27 ppm ($-\text{CH}_2$:32H), 2.08 ppm ($-\text{CH}_2-\text{CH}-\text{SO}_3\text{Na}$:4H), 3.70 ppm ($-\text{O}-\text{CH}_2$:8H), 3.98 ppm ($-\text{CH}_2-\text{CH}-\text{SO}_3\text{Na}$:2H), and 4.30 and 4.53 ppm ($\text{COO}-\text{CH}_2$:4H). All other compounds prepared in this work showed similar spectral data.

In this paper, sodium α -sulfonated fatty acid polyethylene glycol mono- and diesters will be abbreviated as PEG-monoSF and PEG-diSF, respectively.

Measurement of surface-active properties. Krafft points (KP) were determined as the temperature at which the turbidity of a 1 wt% aqueous solution disappeared. CMC values were determined by measuring the spectral change of pinacyanol chloride ($2 \times 10^{-5}\text{M}$) (10,11). Pinacyanol chloride was purchased from Eastman Kodak Co. (Kingsport, TN). Interfacial tension of a 0.1 wt% aqueous surfactant solution was measured by the pendant-drop method in an automatic interfacial tensiometer, made by Kyowa Kaimenkagaku Co., Ltd. (Tokyo, Japan), at 25°C. Foamability was evaluated by a simple shaking test in a glass cylinder at 25°C. Foam stability was expressed as the difference between foam volume after shaking and that after allowing to stand 30 min. Calcium stability was measured by the amount of calcium acetate added to make a 1 wt% surfactant solution turbid at 25°C.

RESULTS AND DISCUSSION

Surface-active properties obtained for PEG-monoSF and PEG-diSF are summarized in Tables 1 and 2, respectively.

Krafft point. The plots of KP value vs. value of m for PEG-monoSF ($n = 1$) and PEG-diSF ($n = 1$) are shown in Figure 1, accompanied by similar data for alkyl sulfonate (12), alkyl sulfate (13), AES ($n = 1$) (14,15), and the methyl ester of sodium α -sulfonated fatty acid (Me-SF) (16).

All PEG-monoSF samples are readily soluble in water, and all KP values are below 0°C, for $m = 10$ –16 and $n = 1$ –35, which are remarkably lower than those of Me-SF with the

TABLE 1
Structures and Properties of PEG-monoSF ($C_mH_{2m+1}CH(SO_3Na)COO(CH_2CH_2O)_nH$)

Structure		Krafft point (°C)	Calcium stability (ppm)	CMC (mM)	Interfacial tension (mN/m)	Foam volume (mL)	
<i>m</i>	<i>n</i>					Initial	After 30 min
10	1	< 0	> 1,800	5.50	10.2	85	52
10	2	< 0	> 1,800	6.50	9.8	91	40
10	3	< 0	> 1,800	7.00	10.0	92	25
10	5	< 0	> 1,800	7.60	10.6	84	4
10	9	< 0	> 1,800	9.00	11.3	70	6
10	14	< 0	> 1,800	10.00	12.3	59	4
10	23	< 0	> 1,800	10.10	12.5	61	12
10	35	< 0	> 1,800	10.10	13.0	33	19
12	1	< 0	> 1,800	1.00	8.8	80	48
12	2	< 0	> 1,800	1.30	8.5	82	41
12	3	< 0	> 1,800	1.70	9.0	82	20
12	5	< 0	> 1,800	1.90	9.7	73	9
12	9	< 0	> 1,800	2.10	10.9	74	5
12	14	< 0	> 1,800	2.20	11.7	64	5
12	23	< 0	> 1,800	2.40	12.4	66	3
12	35	< 0	> 1,800	2.40	12.5	45	8
14	1	< 0	> 1,800	0.30	9.2	68	50
14	2	< 0	> 1,800	0.32	8.6	72	38
14	3	< 0	> 1,800	0.35	8.2	65	21
14	5	< 0	> 1,800	0.37	8.5	55	13
14	9	< 0	> 1,800	0.45	9.5	50	4
14	14	< 0	> 1,800	0.47	10.2	66	7
14	23	< 0	> 1,800	0.48	10.7	76	9
14	35	< 0	> 1,800	0.50	12.0	51	5
16	1	< 0	> 1,800	0.07	10.0	30	28
16	2	< 0	> 1,800	0.08	9.6	35	30
16	3	< 0	> 1,800	0.09	9.0	32	26
16	5	< 0	> 1,800	0.10	8.3	35	24
16	9	< 0	> 1,800	0.11	8.9	28	24
16	14	< 0	> 1,800	0.12	9.8	25	9
16	23	< 0	> 1,800	0.13	10.8	15	7
16	35	< 0	> 1,800	0.13	11.1	21	12

same alkyl chainlength. This result indicates that the introduction of a polyoxyethylene unit into the surfactant molecule as a side chain is effective for reducing the KP value. It was also noteworthy that the KP value of PEG-monoSF ($n = 1$) was about 35°C lower than that of the corresponding AES ($n = 1$) with the same number of EO groups. There are two structural differences between PEG-monoSF and AES. One is the kind of anionic group, that is, sulfonate for PEG-monoSF and sulfate for AES. It is generally known, however, that a sulfonate group gives a higher KP than a sulfate group, as shown in Figure 1 (compare the KP value of alkyl sulfonate with that of alkyl sulfate), and it is assumed that the lower KP value of PEG-monoSF is not caused by this structural difference. The second is the locational difference of the alkyl chain, EO chain, and anionic group in the surfactant molecule. The sulfonate group of PEG-monoSF is located at the same carbon atom as the EO chain. Conversely, the sulfate group of AES is located at the end of the EO chain. In other words, the PEG-monoSF molecule has a branched structure, and the AES molecule has a linear structure. Concerning the KP value of a surfactant such as alkyl sulfate (17), it is well known that the KP value of the branched structure is

much lower than that of the linear structure. Therefore it is assumed that the branched structure of PEG-monoSF drastically lowers the KP value.

KP values of PEG-diSF were below 0°C, except for PEG-diSF ($m = 14, n = 1$) (2°C), PEG-diSF ($m = 16, n = 1$) (23°C), and PEG-diSF ($m = 16, n = 2$) (10°C). KP values of sodium α -sulfonated fatty acid higher-alcohol esters, which had two hydrophobic alkyl chains and one hydrophilic anionic group, were relatively high, as shown in a previous paper (1). PEG-diSF has a very low KP value, however, because it has two hydrophobic alkyl chains and two hydrophilic groups in a molecule. The low KP value of the amphiphiles with double hydrophobic chains and double hydrophilic groups has also been reported by Okahara *et al.* (6–9).

The structure of the PEG-diSF ($n = 1$) molecule behaves as if two Me-SF molecules are combined. The KP value of PEG-diSF ($n = 1$), however, is much lower than Me-SF. This result suggests that the connected oxyethylene side-chain makes the KP value lower by restricting the steric nature of the molecule.

Calcium stability. As shown in Table 1, PEG-monoSF and PEG-diSF have good calcium stabilities, and they are applic-

TABLE 2
Structures and Properties of PEG-diSF ($C_mH_{2m+1}CH(SO_3Na)COO(CH_2CH_2O)_nCOCH(SO_3Na)C_mH_{2m+1}$)

Structure		Krafft point (°C)	Calcium stability (ppm)	CMC (mM)	Interfacial tension (mN/m)	Foam volume (mL)	
<i>m</i>	<i>n</i>					Initial	After 30 min.
10	1	< 0	> 1,800	0.99	9.6	56	40
10	2	< 0	> 1,800	1.05	9.3	45	34
10	3	< 0	> 1,800	1.10	9.5	31	20
10	5	< 0	> 1,800	1.20	9.7	19	2
10	9	< 0	> 1,800	1.30	10.1	20	3
10	14	< 0	> 1,800	1.40	10.8	25	3
10	23	< 0	> 1,800	1.50	11.9	20	7
10	35	< 0	> 1,800	1.50	12.1	22	8
12	1	< 0	> 1,800	0.25	8.2	54	39
12	2	< 0	> 1,800	0.27	7.3	41	35
12	3	< 0	> 1,800	0.29	7.4	35	19
12	5	< 0	> 1,800	0.32	7.6	22	6
12	9	< 0	> 1,800	0.34	8.8	13	10
12	14	< 0	> 1,800	0.36	9.2	14	5
12	23	< 0	> 1,800	0.37	10.2	20	6
12	35	< 0	> 1,800	0.38	10.1	20	3
14	1	< 0	> 1,800	0.072	9.6	50	37
14	2	< 0	> 1,800	0.075	9.4	41	33
14	3	< 0	> 1,800	0.078	8.9	30	21
14	5	< 0	> 1,800	0.085	8.7	16	10
14	9	< 0	> 1,800	0.085	8.6	17	6
14	14	< 0	> 1,800	0.090	8.3	16	6
14	23	< 0	> 1,800	0.096	9.3	15	2
14	35	< 0	> 1,800	0.098	10.0	13	8
16	1	23	950	0.017	10.6	31	30
16	2	10	1,280	0.018	10.5	23	21
16	3	< 0	1,590	0.019	10.4	15	10
16	5	< 0	> 1,800	0.021	10.3	13	7
16	9	< 0	> 1,800	0.022	10.3	10	4
16	14	< 0	> 1,800	0.023	10.2	9	8
16	23	< 0	> 1,800	0.025	9.8	13	6
16	35	< 0	> 1,800	0.026	10.7	8	8

able to many uses in hard water, such as detergents and emulsifiers. These calcium stabilities are much higher than Me-SF, so it is clear that the introduction of a polyoxyethylene unit into the sodium α -sulfonated fatty acid molecule is effective for improvement of calcium stability.

Critical micelle concentration. Plots of CMC vs. *n* value for PEG-monoSF (*m* = 12) and PEG-diSF (*m* = 12) are shown in Figure 2, together with data for AES and alcohol ethoxylate (AE) of corresponding structure (18,19). CMC values of both PEG-monoSF (*m* = 12) and PEG-diSF (*m* = 12,16) gradually increased with increasing number of *n*. The tendency was similar to AE and different from AES. It is well known that the CMC value of AE increases with increasing number of *n*, as a rule, because the hydrated EO unit acts as a hydrophilic group in the aqueous solution. For AES, however, the hydration of the EO unit inserted between the alkyl chain and the sulfate group is only slight, and that EO unit partly behaves as a hydrophobic group in aqueous solution. The CMC value of AES then decreases with an increase in the *n* ≤ 5 (20). Accordingly, it is presumed that the EO unit of PEG-monoSF and PEG-diSF is hydrated and acts as a hydrophilic group in aqueous solution despite the presence of the sul-

fonate group, and the CMC value becomes larger with increasing *n*.

CMC values of PEG-monoSF were smaller than those of AES, when *n* ≤ 5. Furthermore, CMC values of PEG-diSF were smaller by half or one order than those of PEG-monoSF. The well-known Hartley effect (21) explains the small CMC values shown by double-chain amphiphiles. Conventional double-chain amphiphiles, though, are not always favorable for being applied to conventional uses, such as detergents and emulsifiers, because of high KP and poor water solubility. PEG-diSF materials simultaneously have a low KP and small CMC. See Figure 2.

Plots of CMC vs. carbon number of the hydrophobic alkyl group *m* for PEG-monoSF (*n* = 1,3) and PEG-diSF (*n* = 1,3) are shown in Figure 3, along with data for Me-SF (16). CMC values for both PEG-monoSF and PEG-diSF were smaller compared to Me-SF and logarithmically decreased with increasing *m* value. The relationship between CMC and alkyl chainlength is well known (22), as expressed by:

$$\log \text{CMC} = A - Bm \quad [1]$$

where *A* is a specific constant for the particular homologous

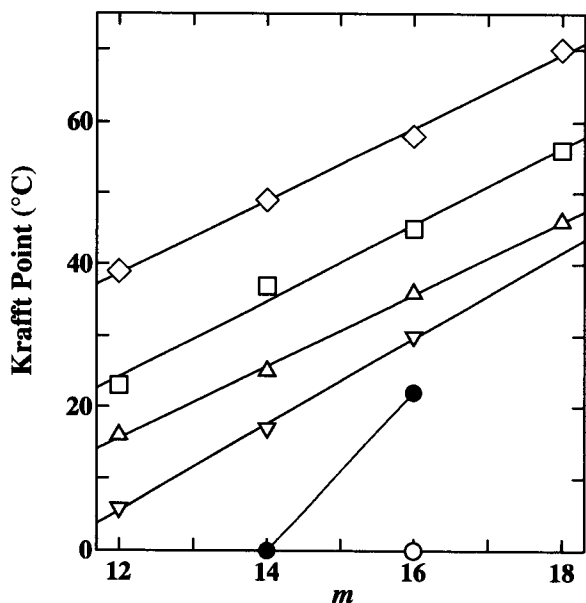


FIG. 1. Relationship between Krafft point and alkyl chainlength of surfactant: \diamond : $C_mH_{2m+1}SO_3Na$, \square : $C_mH_{2m+1}OSO_3Na$, \triangle : $C_mH_{2m+1}O(C_2H_4O)SO_3Na$, ∇ : $C_mH_{2m+1}CH(SO_3Na)COOCH_3$, \circ : $C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)H$, \bullet : $C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)C(=O)CH(SO_3Na)C_mH_{2m+1}$. The Krafft points of PEG-monoSF ($m = 12, 14$) and PEG-diSF ($m = 12$) were below $0^\circ C$.

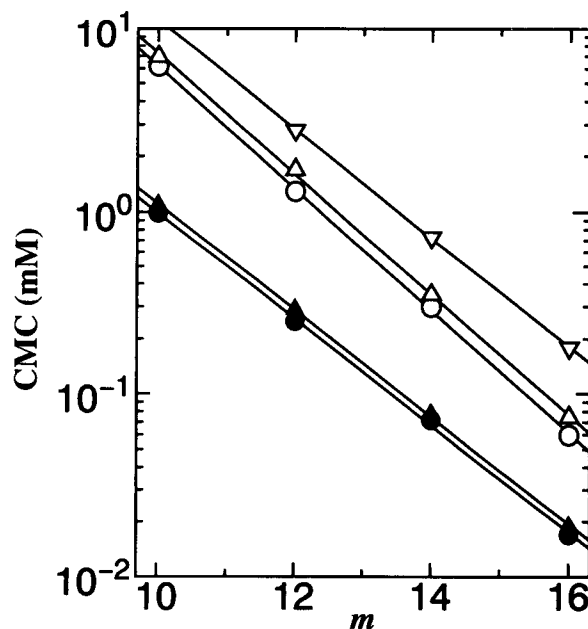


FIG. 3. Relationship between CMC value and alkyl chainlength of surfactant: \circ : $C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)H$, \triangle : $C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)_3H$, \bullet : $C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)C(=O)CH(SO_3Na)C_mH_{2m+1}$, \blacktriangle : $C_mH_{2m+1}CH(SO_3Na)COO(C_2H_4O)_3C(=O)CH(SO_3Na)C_mH_{2m+1}$, ∇ : $C_mH_{2m+1}CH(SO_3Na)COOCH_3$.

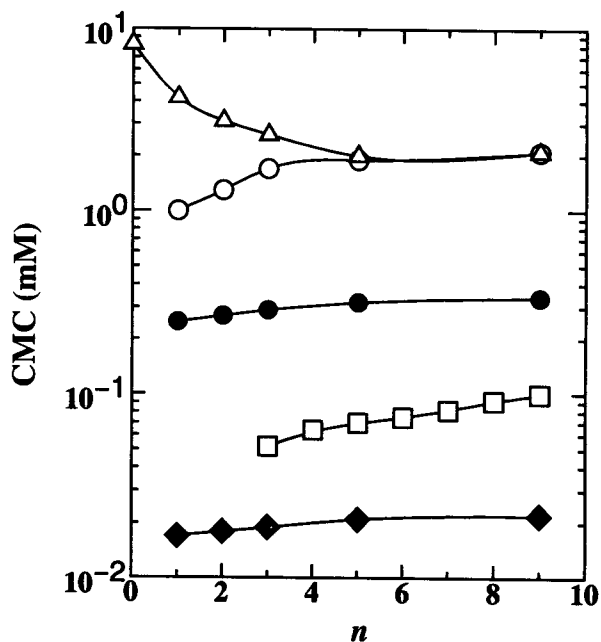


FIG. 2. Relationship between CMC value and EO chainlength of surfactant: \circ : $C_{12}H_{25}CH(SO_3Na)COO(C_2H_4O)_nH$, \bullet : $C_{12}H_{25}CH(SO_3Na)COO(C_2H_4O)_nC(=O)CH(SO_3Na)C_{12}H_{25}$, \blacklozenge : $C_{16}H_{33}CH(SO_3Na)COO(C_2H_4O)_nC(=O)CH(SO_3Na)C_{16}H_{33}$, \triangle : $C_{12}H_{25}O(C_2H_4O)_nSO_3Na$, \square : $C_{12}H_{25}O(C_2H_4O)_nH$.

series and temperature (23,24). B represents the contribution of one methylene group ($-CH_2-$) to the reduction in free energy by micellization, and it is defined by:

$$B = \omega / (1 + K_g) 2.303 kT \quad [2]$$

where ω is the cohesive energy change for transferring one methylene group from a hydrophobic environment to an aqueous medium; K_g , the experimental constant for a particular surface-active agent, which means the electrical repulsive energy change of the anionic group; k , the Boltzmann constant; and T , the absolute temperature.

B values of PEG-monoSF ($n = 1, 3$), PEG-diSF ($n = 1, 3$), and some surfactants (23) are listed in Table 3. The B value of PEG-monoSF ($n = 1$) was 0.324, and that of PEG-monoSF ($n = 3$) was 0.336. These values are somewhat larger than those of typical anionic surfactants such as sodium alkyl sulfate. This suggests that PEG-monoSF micelles have a relatively strong cohesive force or a weak electrical repulsive force. From a steric view of the molecular structure, PEG-monoSF has a relatively large hydrophilic group compared to sodium alkyl sulfate. For such a cone-type surfactant micelle, the large hydrophilic group occupies a large area in the vicinity of the head group, and hydrophobic alkyl chains are allowed to assemble closely in the core (25). It is then assumed that the ω value of PEG-monoSF is smaller than that of other surfactants. Moreover, the PEG unit of PEG-monoSF is readily hydrated and behaves as a hydrophilic group in aqueous solution, as already described. Then the anionic electrical charge of the hydrophilic group is apparently weakened, and the electrical repulsive energy change of the anionic group (K_g value) may be reduced. As a result, the B value of PEG-monoSF is larger than those of the others.

TABLE 3
B Values of PEG-monoSF, PEG-diSF, and Other Surfactants

Surfactant	Temperature (°C)	B value	Measurement	
			Method ^a	Reference
PEG-monoSF (<i>n</i> = 1)	25	0.324	A	This work
PEG-monoSF (<i>n</i> = 3)	25	0.336	A	This work
PEG-diSF (<i>n</i> = 1)	25	0.294	A	This work
PEG-diSF (<i>n</i> = 3)	25	0.294	A	This work
RCOOK	25	0.290	A,B	(26,27)
	45	0.292	B	(27)
RCH(COOK) ₂	25	0.220	A,E	(28)
RSO ₃ Na	40	0.294	B,C,	(27,29)
	50	0.294	B,C	(27,29)
RSO ₄ Na	45	0.295	A,B	(30)
Na 2-alkylbenzene sulfonate	55	0.292	A	(31)
Alkyl glucoside	25	0.530	D	(32)

^aA = dye method, B = refraction method, C = conductivity method, D = surface-tension method, and E = solubilization method.

Conversely, *B* values of PEG-diSF (*n* = 1,3) were 0.294, being the same as those of conventional surfactants, such as AS and AES. This result suggests that the steric structure of PEG-diSF, which consists of two hydrophilic groups and two hydrophobic chains, is similar to AS and AES, and the ω and K_g values of PEG-diSF are the same.

Interfacial tension. Interfacial tensions between 1 wt% aqueous solutions of PEG-monoSF and soybean oil clearly depend on the *m* and *n* values. Especially, the effect of *n* was evident, and low interfacial tensions were obtained when *n* was relatively small. When the *m* value was different, a minimum interfacial tension was obtained for different *n* values: *n* = 2 *m* = 12; *n* = 3 when *m* = 14; and *n* = 5 when *m* = 16. The minimum value of interfacial tension, however, was not affected by *m*, and those values were about 8.3 mN/m in each structure.

Conversely, PEG-diSF showed a lower interfacial tension than PEG-monoSF with the same *m* and *n* values. Interfacial tensions between 1 wt% aqueous solutions of PEG-diSF and soybean oil also depended on *m* and *n*, and their tendency was similar to PEG-monoSF. For *m* = 12, the minimum interfacial tension was obtained when *n* = 2, and the value was 7.2 mN/m.

Foaming properties. Foam volumes of PEG-monoSF evidently depend on *m* and *n* values, as shown in Table 1. Initial foam volume decreased gradually with increasing *m* and *n* values. For *m* = 12, foam volumes of more than 80 mL were observed when *n* was less than 3. This foamability is similar to that of sodium dodecyl sulfate, whose foam volume was 80 mL, and higher than sodium dodecyl ethoxy (*n* = 3) sulfate with a foam volume of 63 mL. It is noteworthy that foams made from PEG-monoSF started to decrease rapidly. For example, the initial foam volume of PEG-monoSF (*m* = 12, *n* = 9) was 70 mL, but it decreased to 5 mL after 30 min. It is generally well known that most conventional anionic surfactants, such as sodium dodecyl sulfate (80 mL after 30 min) and sodium dodecyl ethoxy (*n* = 3) sulfate (60 mL after 30 min), have good foamability as well as good foam stability. In con-

trast to them, PEG-monoSF has good foamability, but low foam stability.

Foam volumes for PEG-diSF were also dependent on the *m* and *n* values, and the tendency of this structural effect was similar to PEG-monoSF (Table 2). The foam volumes of PEG-diSF, though, were relatively lower than those of PEG-monoSF. The outstanding foaming property of PEG-diSF is certainly its low foaming ability.

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